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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 2/44, 255/02, H01B 3/44	A1	(11) International Publication Number: WO 94/14852 (43) International Publication Date: 7 July 1994 (07.07.94)
(21) International Application Number: PCT/US93/11682 (22) International Filing Date: 2 December 1993 (02.12.93)		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 07/997,074 29 December 1992 (29.12.92) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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(54) Title: HALOGEN-FREE FLAME RETARDANT COMPOSITIONS		
(57) Abstract		
A halogen-free composition comprising 100 parts of polyolefin resin grafted with from 1 to 10 parts maleic anhydride; from 0.1 part to 10 parts of a free radical catalyst therefor, from 0.5 part to 10 parts of an antioxidant, and from 5 parts to 500 parts of at least one ammonium polyphosphate containing flame retardant, and articles made therefrom, including halogen-free electrical tape backings.		

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HALOGEN-FREE FLAME RETARDANT COMPOSITIONSBackground of the InventionField of the Invention

5 The invention relates to heat shrinkable, filled polymer compositions containing halogen-free flame retardant components suitable for use in electrical applications.

10 Description of the Related Art

Heat-shrinkable components, e.g., extruded or molded products, have been widely used in electrical applications. In a series of publications, Hoffman et al, disclose a range of uses in electrical insulation and environmental protection, from low voltage to high voltage installations. *Insulation Enhancement with Heat-Shrinkable Components* - J.W.Hoffman and others, IEEE Electrical Insulation Magazine, Part I, March/April 1991 Vol. 7, No.2, page 33; Part II, May/June 1991 Vol. 7, No.3, page 16; Part III, July/August 1991 Vol. 7, No.4, page 31.

Among the various requirements for satisfactory performance, these authors frequently emphasize the need for superior electrical insulation and prevention of moisture attack. The latter is accomplished either by the use of hydrophobic sealant materials or by the intentional incorporation of hydrophobic species in the heat-shrinkable compositions.

Another requirement specified for heat-shrinkable polymers is the requirement that they be semi-crystalline polymers. The most common class of semicrystalline polymers includes polyolefins. Therefore polyolefins have tended to be materials of choice for the manufacture of heat-shrink products. Polyolefin polymers containing additives such as flame retardants have been extensively disclosed in the prior art. See, for example, U.S. Pat.

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4,174,343; JP 54,022,450; JP 54,007,451; JP 54,004,946; U.S. Pat. 3,810,862; EP 494,778; U.S. Pat. 5,116,891; U.S. Pat. 4,997,876; U.S. Pat. 4,871,795; U.S. Pat. 4,727,102 and US 4,772,642. Flame retardants disclosed
5 include such inorganic additives as magnesium hydroxide, calcium hydroxide, aluminum hydroxide, alkali phosphates and ammonium polyphosphate. Flame retardancy of these materials may be augmented using organic compounds including those containing halogen compounds. Other
10 references disclose modified polyolefins. Modification is usually accomplished by the grafting of a selected functionality at intervals along the backbone of the polyolefin polymer. Suitable polymers in this category are generally acid modified polyolefins produced by
15 reaction with, e.g., an unsaturated carboxylic acid or derivative thereof.

Japanese patent JP 1,108,241 discloses polyolefins grafted with a variety of acid species, including maleic acid, maleic anhydride, fumaric acid, acrylic acid etc..
20 Flame retardant compositions, based on these modified polymers, are disclosed. The preferred additives used to impart flame retardancy include aluminum hydroxide, magnesium hydroxide, magnesium carbonate, calcium hydroxide, and the like. JP 2,284,940 discloses that the
25 bending strength of a polyolefin modified with acrylic acid or maleic anhydride was approximately three times greater than the unmodified polymer. Flame retardant was added to the acid-modified polyolefin, the use of ammonium polyphosphate was not disclosed. Further, there
30 was no teaching or suggestion that higher amounts of additives of this type could be accommodated.

Other references cite similar compositions, including JP 1,172440; JP 62,235,343; JP 62,011,745; U.S. Pat. 4,722,858. However, none of the modified polyolefin
35 references disclose the use of ammonium polyphosphate containing compositions. There is no suggestion of the use of ammonium polyphosphate in compositions and

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structures used to provide electrical insulation and environmental protection, especially moisture protection.

The reason for the rejection of ammonium polyphosphate in electrically insulating or moisture repellent compositions is due to the fact that ammonium polyphosphate readily absorbs water. Thus it inherently attracts moisture which interferes with the effectiveness of electrical insulation and contact integrity at the site of an electrical connection. One reference, U.S. Pat. 4,772,642, attempts to solve the problem by encapsulating ammonium polyphosphate in a water-insoluble synthetic resin to produce a more water-stable fire-retardant composition. However, this is expensive to accomplish.

Similarly, U.S. Pat. 5,071,901 discloses the use of quaternary ammonium salts for modifying the surface of ammonium polyphosphate. This patent states that electrical insulation containing ammonium polyphosphate is generally deficient in water resistance. Therefore a surface treatment is needed to prevent leaching of ammonium polyphosphate from polymeric insulating materials, such as polyolefins, to which it may be added. It is stated that if leaching occurs, the electrical insulation and fire retardant performance will suffer.

The use of ammonium polyphosphate in heat shrinkable structures including tubes and molded shapes has been disclosed in United States patent U.S. 4,223,071. This patent discloses the use of ammonium polyphosphate as one of a series of phosphorus containing compounds used for erosion control of insulators for high voltage lines. No reference is made to its use in high performance insulation of electrical wiring or as a flame retardant.

The present inventor has discovered a combination of materials which will allow the use of ammonium polyphosphate in halogen-free flame retardant containing polymer compositions suitable for use where electrical insulation is of primary importance. In addition, the

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compositions of this invention can accommodate significantly higher quantities of flame retardant than that previously disclosed. The present invention provides compositions which take advantage of the 5 superior flame retardancy of ammonium polyphosphate, while significantly reducing its tendency to attract water or water vapor. This is accomplished without any special surface treatment of the ammonium polyphosphate particles. Compositions of the current invention are 10 therefore effective in preventing the common phenomenon of water leaching of ammonium polyphosphate from the polymer matrix. Additionally it has been discovered that flame retardancy is further enhanced by the incorporation of higher levels of flame retardant than was previously 15 thought possible. This is accomplished without loss of mechanical performance of the polymer compositions.

These compositions are especially useful for flame retardant tape backings, such as those utilized in the electrical industry.

20 These compositions are also useful for flame retardant heat-shrink extruded or molded products for the electrical industry.

Summary of the Invention

25 The present invention provides halogen-free polyolefin compositions containing flame retardant additives. These polyolefin compositions are useful for tape backings and extruded or molded heat-shrink components for use in electrical applications.

30 Compositions of the invention use graft-modified polyolefin polymers and copolymers derived from polyolefins. The resulting graft polymers are then combined with additives in compositions which have improved mechanical properties and high flame retardancy.

35 Surprisingly, use of the acid-modified polyolefin and the hydrophilic flame retardant appears to have a synergistic effect, such that the ammonium polyphosphate

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appears to be rendered inaccessible to water. Thus, it does not cause the expected deterioration of electrical properties associated with compositions of the prior art. This makes it possible to provide heat-shrinkable tapes 5 and molded or extruded shapes using compositions comprising acid-modified polyolefin polymers or modified ethylene copolymers, an antioxidant and a combination of flame retardant materials.

Specifically, halogen-free compositions of the 10 invention comprise 100 parts of polyolefin resin grafted with from 1 to 10 parts maleic anhydride; from 0.1 part to 10 parts of a free radical catalyst therefor, from 0.5 part to 10 parts of an antioxidant, and from 5 parts to 500 parts of at least one ammonium polyphosphate 15 containing flame retardant.

One embodiment of the invention comprises a halogen-free heat-shrink article comprising 100 parts of polyolefin resin grafted with from 1 to 10 parts maleic anhydride, from 0.1 part to 5 parts organic peroxide 20 catalyst, from 0.5 parts to 10 parts of an antioxidant, and from 5 parts to 500 parts of an ammonium polyphosphate containing flame retardant.

Preferred compositions of the invention are halogen-free electrical tape backings comprising 100 parts of polyolefin resin grafted with from 1 to 10 parts maleic anhydride, from 0.1 part to 5 parts organic peroxide catalyst, from 0.5 parts to 10 parts of an antioxidant, and from 5 parts to 500 parts of an ammonium 25 polyphosphate containing flame retardant.

All compositions within the scope of the invention 30 successfully passed UL-94, V-0 flame test using a specimen thickness of 0.08 cm to 0.16 cm.

As used herein, the term "original polyolefin polymer" refers to the polyolefin polymer prior to the 35 graft conversion reaction, or the addition of any ingredients for such reaction.

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Detailed Description of the Invention

In the selection of polymers to be used in electrical applications, there are at least three conditions which must be met. The first requirement is 5 the need for high insulation resistance. Second, is the need for low dielectric constant. Third, prevention of attraction of the composition for moisture and other negative species, which facilitate formation of ionic charge carriers. For electrical applications, the most 10 useful combination of properties is found in polymers of the polyolefin family. Commonly used polymers include, polyethylene (LDPE, LLDPE, and the like); poly(ethylene-ethyl-acrylate); poly(ethylene-vinyl-acetate); 15 poly(ethylene-methyl-acrylate); chlorinated polyethylene and blends thereof.

Preferred polymers include linear low density polyethylene, (LLDPE), available as "Dowlex-2047A" from Dow Chemical Co., and ethylene-vinyl-acetate, available 20 as Elvax™ 460 or Elvax™ 470 from DuPont. Graft polymers of these homopolymers or copolymers are prepared using maleic anhydride in the presence of a suitable free-radical initiator.

Compositions of the invention are grafted with from 25 1 to 10 parts of maleic anhydride, preferably from 2 to 7 parts.

Useful free-radical initiators include those which are normally suitable for free-radical polymerization of polyolefins such as organic peroxides, e.g., lauryl 30 peroxide, dicumyl peroxide, benzoyl peroxide, and thermal initiators e.g., 2,2'-azobisisbutyronitrile, commercially available from DuPont under the trade name Vazo™ 64. The initiator comprises from 0.1 to 10 parts per hundred parts original polyolefin polymer, preferably 35 from 1 to 5 parts.

Compositions of the invention also comprise an antioxidant. The antioxidant is useful in amounts of

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from 0.5 parts to 10 parts per hundred parts original polyolefin resin. Useful antioxidants include 2,5 tertiary amyl hydroquinone, tertiary butyl hydroxytoluene, and thio-bis(t-butyl m-cresol), available 5 as Santonox-R™ from Monsanto.

Compositions of the invention further comprise a flame retardant additive. Useful flame retardants include inorganic oxides, hydroxides and phosphates, as well as those containing ammonium polyphosphate, e.g. 10 Exolit™ IFR-10, Exolit™ IFR-23 and Exolit™ IFR-422, all of which are available from Hoechst-Celanese. An organic co-reagent is usually added in combination with the inorganic materials. It is important to note that the flame retardant additives are not subjected to any 15 special treatment to reduce sensitivity to moisture or water solubility. An additional non ammonium polyphosphate containing flame retardant may also be present.

Surprisingly large amounts of flame-retardant may be 20 added to acid modified polyolefins without detrimental effect upon the physical properties of the polymer. Physical property improvement of grafted polyolefins over standard polyolefins has been observed previously. However, it is surprising that such improvement would 25 allow the inclusion of greater amounts of flame retardant materials without losing said improved characteristics. Ammonium polyphosphate containing flame retardant additives comprise from 5 parts to 500 parts per 100 parts original polyolefin resin, preferably from 25 parts 30 to 250 parts, most preferably from 60 parts to 125 parts.

Compositions of the invention may further comprise additional adjuvants. Classes of additives typically employed include, inert fillers, couplers, plasticizers, UV stabilizers, antioxidants, curing agents and other 35 useful additives, in minor amounts which do not change the essential nature of the composition.

Compositions of the current invention utilize the

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minimum number of required components while providing highly effective electrically insulating, flame retarding materials.

The polyolefin compositions of the invention are
5 useful for tape backings and extruded or molded heat-shrink components for use in electrical applications. The flame retardant properties are retained in the resulting tape backings, and in extruded and molded heat-shrink products made therefrom.

10 For example, a tape backing of the invention may be coated with an adhesive, and used for electrical insulating tape. Extruded and molded heat-shrink products are useful as protective electrically insulating covers, in an electrical cable splicing operation. Since
15 the compositions include polyolefins, which are semi-crystalline polymers, conventional processing techniques may be used to form the heat-shrinkable products such as tapes and shapes.

20 The following examples provide compositions which demonstrate outstanding electrical insulation and flame retardancy performance while incorporating quantities of additives previously viewed as detrimental to performance characteristics.

25 Quantities of materials are expressed in terms of parts per hundred (pph) based upon the original 100 parts of polyolefin resin prior to reaction with grafting components. Therefore, all compositions are presented with components defined in parts per hundred of the original resin.

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Examples

Glossary of Materials

APP	Ammonium Polyphosphate
Dowlex™-2047A	Linear Low Density Polyethylene
5 Elvax™ 460	Ethylene Vinyl Acetate
Elvax™ 470	Ethylene Vinyl Acetate
DPD - 6169	Ethylene Ethyl Acrylate
10 Exolit™ IFR-10	Intumescent Flame Retardant (66% APP)
Exolit™ IFR-23	Intumescent Flame Retardant (80% APP)
Exolit™ IFR-422	Intumescent Flame Retardant (100% APP)
15 Santonox™ R	Thio-bis(t-butyl m-cresol)
Maleic Anhydride	99% Maleic Anhydride
Dicup™ 40KE	Dicumyl Peroxide (40% in CaCO ₃)
Dicup™ R	Dicumyl Peroxide (99%)

Examples 1 and 2

The following information describes a general preparation for compositions useful in the invention. Examples 1 and 2 differ in the level of maleic anhydride grafts present in the modified polyolefin polymers.

25

	<u>Example 1</u>	<u>Example 2</u>
Polymer	100 parts	100 parts
Maleic Anhydride	2.0	4.0
Dicup™ 40KE	1.0	2.0
30 Santonox™ R	3.8	3.8
Exolit™ IFR-23	130.5	134.2

Part A - Maleic Anhydride Grafting

The grafting reaction and mixing with flame retardant were conducted in sequence on a Haake Rheomix™ with a constant mixing speed of 50 rpm. Polymer was fluxed at 135°C (275°F) for one minute and then maleic anhydride and dicumyl peroxide were simultaneously added. The mixing process was continued for two minutes and then 40 Santonox R™ was added. Santonox R™ has two purposes. It

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is first used to quench the free radical grafting reaction, after which any excess acts as a protective antioxidant for the composition.

5 Part B - Addition of Flame Retardant

The temperature of the grafted polymer was raised to 199°C (390°F). At this temperature the polymer is molten and the flame retardant may be readily mixed into the composition. Thereafter, mixing of the composition was 10 continued for three to four minutes to ensure satisfactory distribution of the flame retardant.

Sample Preparation

15 The compositions were molded into plaques 15.2 cm square and 0.078 cm thick at a molding temperature of 163°C (325°F). The mechanical properties of these samples were tested according to ASTM D638. Table 1 shows typical results using Elvax™ 470 as the polymer matrix. Table 2 shows the results of using different 20 polymer matrices.

Comparative Example 3

Using the same equipment and conditions outlined in Examples 1 and 2, flame retardant Exolit™ IFR-23 was 25 added to polymers which were not subjected to maleic anhydride grafting. The results for this comparative composition are also presented in Table 1.

Table 1

Ex No	Exolit™ IFR-23 pph	Tensile Strength MPa	Elongation at Break %
1	130.5	11.90	605
2	134.2	14.42	610
3A	126.8	9.75	530

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Examples 4-8 and 4C-8C

Examples 4-8 were made as described in Example 1, with each composition have 2 pph grafting, and Comparative Examples 4C-8C were made as described in Example 3C with no grafting. Various polyolefin resins were used.

Table 2

Ex No	Polyolefin Resin	Exolit™ IFR pph	Tensile Strength MPa	Elongation at Break %
4	Elvax™ 460	130.5	8.03	545
4C	Elvax™ 460	126.8	5.77	410
5	Elvax™ 470	130.5	11.90	605
5C	Elvax™ 470	126.8	9.75	530
6	Dowlex™ 2047A	130.5	10.72	420
6C	Dowlex™ 2047A	126.8	6.43	130
7	DPD-6169	130.5	9.25	650
7C	DPD-6169	126.8	7.35	585
8	Blend*	130.5	11.30	570
8C	Blend*	126.8	9.75	510

* Blend 50/50 = 50 parts Elvax™ 470 + 50 parts grafted Elvax™ 470.

25

Examples 9-17

Grafted polyolefin polymers comprising 100 pph Elvax™ 470, 3.5 pph maleic anhydride, 3.0 pph Dicup-40KE and 4.2pph Santonox R were prepared according to Example 1, part A. Increasing amounts of Exolit™ IFR - 23, containing ammonium polyphosphate, were added to the grafted polymer as described in Example 1, part B.

Physical properties of these compositions are provided in Table 3. There is clear evidence that the properties of compositions containing grafted polyolefin

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polymers consistently exceed those where non-grafted polymers are used. In Examples 9-17, 100 parts of Elvax™ 470 were used. Table 3 shows the physical properties and the changes in those properties as the Exolit™ IFR-23 amount is varied.

Table 3

Ex No	Exolit™ IFR-23 pph	Polymer Type	Tensile Strength MPa	Elongation at Break %
9	5.8	Control	24.30	800
		Grafted	24.99	825
10	12.3	Control	22.41	760
		Grafted	23.96	810
11	27.6	Control	18.96	700
		Grafted	21.20	760
12	47.4	Control	15.69	650
		Grafted	18.62	720
13	78.3	Control	13.10	600
		Grafted	15.86	670
14	110.7	Control	10.69	550
		Grafted	13.27	630
15	166.1	Control	8.27	425
		Grafted	10.68	465
16	258.3	Control	6.21	300
		Grafted	7.93	345
17	442.8	Control	3.96	160
		Grafted	5.17	200

Water Immersion Tests

The insulation resistance was measured for a heat shrink material composition according to the Example 9 (50% Exolit™ IFR-23). Measurements (ASTM D-257) were made initially and after samples had been immersed in

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water, maintained at 23°C, for increasing periods of time. Results of the water immersion test are shown in Table 4.

5

Table 4

Insulation Resistance (Ohm-cm)		
Water Immersion (days)	Control (no grafting)	Grafted Elvax™
10	0	5.4×10^9
	1	4.2×10^5
	3	4.8×10^4
	7	Below 10^3
		1.0×10^{14}
		3.8×10^{12}
		3.0×10^{11}
		2.8×10^{10}

15

A second water immersion test was performed to determine the amount of water which formulations, containing various levels of maleic anhydride grafts, absorb when submerged in water, at room temperature, for 20 a period of twenty-four hours.

20

Examples 18-21

Table 5 shows varied compositions of the invention; table 6 shows the amount of water absorbed for various amounts of graft-modified polyolefin resin. Water absorption is reported in Table 6 as function of weight gained during immersion. Reduction in water uptake is clearly affected by the amount of maleic anhydride (see Examples 13-16) incorporated into the polyolefin by grafting. In Examples 18-21, there were 100 parts of Elvax™ 470, with the following additives.

25

30

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Table 5

Ex No	Maleic Anhydride pph	Dicup™ 40KE pph	Santonox™R pph	Exolit™ IFR-23 pph
5 18	0	0.86	1.19	102
19	3.5	3.01	4.17	110.7
20	4.8	4.13	5.71	114.6
21	6.0	5.16	7.14	118.3

10

Table 6

Ex No	Amount of Grafting pph	Water Absorption Wt%
18	0	11.9
15 19	3.5	5.7
20	4.8	3.9
21	6.0	2.9

20

Examples 21-25

The dielectric constant of various electrically insulating compositions was measured for compositions containing polyolefin polymers with and without grafting. The compositions varied according to the amounts of 25 flame-retardant (Exolit™ IFR-23) added. In Examples 21-25, there were 100 parts of Elvax™ 470 with the following additives.

Table 7 shows the formulations of compositions of the invention in which the amount of flame retardant is 30 varied; Table 8 shows the dielectric constant for each of the compositions.

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Table 7

Ex No	Maleic Anhydride pph	Dicup™ 40-KE pph	Santonox™R pph	Exolit™ IFR-23 pph
5	21	3.5	3.0	4.2
	22	3.5	3.0	4.2
	23	3.5	3.0	4.2
	24	3.5	3.0	4.2
	25	3.5	3.0	4.2

10

Table 8

Ex No	Exolit™ IFR-23 pph	Elvax™ 470 Control	Grafted Elvax™ 470 (3.5 pph M.A.)
15	21	3.05	2.85
	21	3.2	3.0
	23	3.7	3.35
	24	4.1	3.5
	25	5.1	3.65

25

A flame retardant composition was prepared according to Example 14, wherein the ammonium polyphosphate was replaced by magnesium hydroxide. The mechanical properties are shown in Table 9 and the water immersion testing results are shown in Table 10.

30

Table 9

	Control	Grafted
Tensile Str. (MPa)	9.13	12.34
Elongn. at Break (%)	150	202
Water Absorption (Wt.%)	0.43	1.77

35

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Table 10

Insulation Resistance (Ohm-cm)		
Water Immersion (days)	Control	Grafted
0 (Dried)	5.0×10^{15}	4.4×10^{15}
1	4.2×10^{13}	5.1×10^{12}
3	1.2×10^{12}	6.9×10^{10}
7	3.3×10^{11}	2.4×10^{10}

10

Example 27

A composition having the formulation 100 parts of Elvax™ 470, 5.0 parts of maleic anhydride, 1.7 parts Dicup™-R, and 5.9 parts Santonox™ R was used to prepare a grafted polymer using reactive extrusion techniques. The components were combined in a twin screw extruder operating at 120°C. Residence time at this temperature was 33 seconds. Polymer from the reactive extrusion process was transferred to a Banbury mixer operating at 199°C.

To 100 parts of the grafted polymer was then added 100 parts of Exolit™ IFR-2300, 4.6 parts trimethylol-propane triacrylate, 3.0 parts Irganox™ 1010, and 1.0 part Irganox™ 1024.

The resultant composition was charged into an extruder to produce tubing with an internal diameter of 0.317 cm and a wall thickness of 0.0635 cm. This tubing was subjected to electron beam irradiation of 8.0 Megarads. Thereafter it was heated and expanded to dimensions which were twice those of the unexpanded tubing.

The resulting tube displays heat-shrink properties when heated to a suitable temperature. Measurement of physical, electrical and flame retardant properties confirmed that this tubing is extremely effective in protecting and electrically insulating spliced connections. Its effectiveness for flame retardancy is

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shown by its capacity to withstand the rigorous UL-224,
VW-1 flammability test. At the high particulate loading
of approximately 50%, the composition used for heat
shrink tubing exhibited tensile strength of 14.71 MPa and
5 elongation at break of 710%. Other tests associated with
UL-224, such as insulation resistance and heat aging,
were easily passed by the heat shrink tubing described
here.

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What is Claimed is:

1. A halogen-free composition comprising 100 parts of polyolefin resin grafted with from 1 to 10 parts maleic anhydride; from 0.1 part to 10 parts of a free radical catalyst therefor, from 0.5 part to 10 parts of an antioxidant, and from 5 parts to 500 parts of at least one ammonium polyphosphate containing flame retardant.
2. A halogen-free composition comprising 100 parts of polyolefin resin grafted with from 2 to 7 parts maleic anhydride; from 0.1 part to 5 parts organic peroxide catalyst, from 0.5 parts to 10 parts of an antioxidant selected from the group consisting of phenols, amines, quinoline, imidazole, phosphite, thiol and cyanurate, and from 5 parts to 500 parts of an ammonium polyphosphate containing flame retardant.
3. A halogen-free composition according to claim 2 wherein said polyolefin resin is selected from the group consisting of polyethylene, polypropylene, ethylene vinyl acetate, ethylene ethyl acrylate, ethylene methyl acrylate, ethylene-polypropylene, propylene rubber and mixtures thereof.
4. A halogen-free electrical tape backing having a composition according to claim 1.
5. A halogen-free electrical tape backing having a composition according to claim 3.
6. A halogen-free heat-shrink article having a composition according to claim 1.
7. A halogen-free heat-shrink article having a composition according to claim 3.

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8. A halogen-free heat-shrink article according to
claim 6 wherein said article was formed by a process
selected from extrusion and molding.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/11682

A. CLASSIFICATION OF SUBJECT MATTER IPC 5 C08F2/44 C08F255/02 H01B3/44		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08F H01B C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 091 666 (MONSANTO) 14 January 1972 see page 3, line 19 - line 31 see page 7, line 28 - line 30 see page 12, line 8; claim 1 ---	1-8
X,P	Section Ch, Week 9342, Derwent Publications Ltd., London, GB; Class C08, AN 93-331533 'flame-resistant cyclic olefin-type resin compsn including polyammonium phosphate...' & JP,A,5 239 284 (MITSUI PETROCHEM) 17 September 1993 see abstract ---	1-3
A	EP,A,0 391 336 (CHISSO CORP.) 10 October 1990 see page 5, line 36 - line 37; claims 1-3 ---	1-8 -/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
<p>* Special categories of cited documents :</p> <p>'A' document defining the general state of the art which is not considered to be of particular relevance</p> <p>'E' earlier document but published on or after the international filing date</p> <p>'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>'O' document referring to an oral disclosure, use, exhibition or other means</p> <p>'P' document published prior to the international filing date but later than the priority date claimed</p> <p>'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>'&' document member of the same patent family</p>		
Date of the actual completion of the international search 14 April 1994	Date of mailing of the international search report 04.05.94	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentstaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Loiselet-Taisne, S	

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